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Half-sandwich complexes of titanium and zirconium with pendant phenyl substituents. The influence of *ansa*-aryl coordination on the polymerisation activity of half-sandwich catalysts

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Abstract

Benzyl-substituted Group 4 half-sandwich complexes ($\eta^5\text{-C}_5\text{H}_4\text{R})\text{TiCl}_3$ (**1a**, $\text{R} = \text{CMe}_2\text{Ph}$; **2a**, $\text{R} = \text{CMe}_2\text{CH}_2\text{Ph}$; **4a**, $\text{R} = \text{SiMe}_2\text{Ph}$; **5a**, $\text{R} = \text{CHPh}_2$) are readily accessible from $\text{C}_5\text{H}_4(\text{R})\text{SiMe}_3$ and TiCl_4 , while the reaction of $\text{C}_5\text{H}_4(\text{CMe}_2\text{CH}_2\text{Ph})\text{SiMe}_3$ with $\text{ZrCl}_4(\text{SMe}_2)_2$ affords $(\text{C}_5\text{H}_4\text{CMe}_2\text{CH}_2\text{Ph})\text{ZrCl}_3\cdot\text{dme}$ (**3a**). The structures of **1a**, **4a** and **5a** have been determined by X-ray diffraction; the compounds are monomeric in the solid state. Alkylation readily affords the corresponding trimethyl and tribenzyl derivatives; the crystal structure of $(\eta^5\text{-C}_5\text{H}_4\text{CHPh}_2)\text{Ti}(\text{CH}_2\text{Ph})_3$ (**5b**) has been determined. Treatment of $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{MMe}_3$ with $[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ in dichloromethane at low temperatures generates cationic $[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{MMe}_3]^+$ complexes; the complexes are stabilised by π -coordination to the phenyl ring to give *ansa*-arene complexes with one- and two-carbon linkages. The complexes catalyse the polymerisation of propene. Compared to the system $\text{Cp}^*\text{TiMe}_3/\text{B}(\text{C}_6\text{F}_5)_3$, the *ansa* complexes show reduced catalytic activity and enhanced chain termination. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Titanium; Zirconium; *Ansa*; Polymerisation catalysis; Half-sandwich

1. Introduction

As part of a study of the factors that affect the reactivity and catalytic activity of cationic Group 4 cyclopentadienyl complexes [1], we have recently documented the ability of benzyl substituents to stabilise electrophilic metal centres through π -coordination of benzylic aryl substituents [2]. In the case of bis(cyclopentadienyl) complexes such interactions presumably involve η^2 -coordination [3], similar to the $\eta^2\text{-C}=\text{C}$ coordination detected in zirconocene complexes with alkenyl-substituted cyclopentadienyl ligands [4]. Half-sandwich complexes, on the other hand, are capable of much stronger arene binding. Examples include coordination to phenyl groups of borate anions [5–7] and η^6 -coordination of neutral arenes [8], as well as the formation of *ansa*-metallocene complexes $\{[\text{C}_5\text{Me}_4\text{CH}_2\text{-}$

$\text{CH}_2(\eta\text{-C}_6\text{H}_5)]\text{TiMe}_2\}\text{B}(\text{C}_6\text{F}_5)_4\}$ reported by Flores et al. [9]. We found recently that $\text{Cp}^*\text{TiMe}_3/\text{B}(\text{C}_6\text{F}_5)_3$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$) give highly active catalysts for the polymerisation of propene to atactic elastomeric polypropene of unusually high molecular weight ($\bar{M}_w \approx 1\text{--}4 \times 10^6$) [10,11] and became interested in the possibility of using phenyl coordination to control both catalytic activity and polymer molecular weight. We report here the synthesis of new titanium and zirconium half-sandwich complexes with benzyl substituted cyclopentadienyl ligands and the formation of cationic complexes with *ansa*-aryl structure.

2. Results and discussion

Cyclopentadienyl ligands with $-\text{CMe}_2\text{Ph}$ and $-\text{CMe}_2\text{CH}_2\text{Ph}$ substituents are readily accessible from the reaction of dimethylfulvene with phenyllithium and benzylmagnesium bromide, respectively. Quenching of

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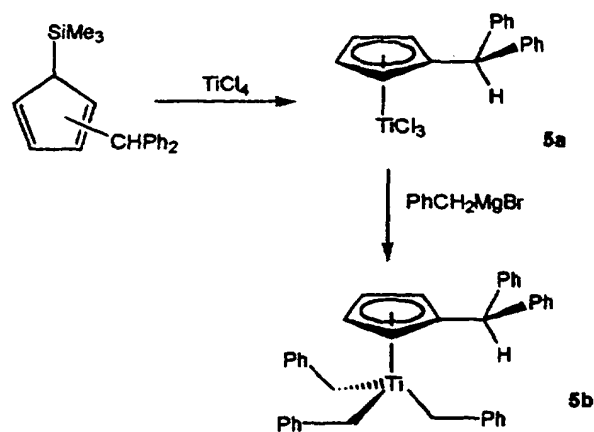
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the resulting lithium or magnesium cyclopentadienides with an excess of trimethylchlorosilane gave good yields of $(C_5H_4SiMe_3)CMe_2Ph$ and $(C_5H_4SiMe_3)CMe_2CH_2Ph$ as pale-yellow oils, which were used for subsequent reactions without further purification. The compound $C_5H_4SiMe_2Ph$ was prepared from sodium cyclopentadienide and dimethylphenylchlorosilane in 82% yield.

The reaction of $(C_5H_4SiMe_3)CMe_2Ph$ with $TiCl_4$ in CH_2Cl_2 at room temperature (r.t.) readily affords $(C_5H_4CMe_2Ph)TiCl_3$ (**1a**) as orange crystals (Scheme 1). The compound $(C_5H_4CMe_2CH_2Ph)TiCl_3$ (**2a**) was made similarly as a dark-red oil, which could not be induced to crystallise. The reaction of $(C_5H_4SiMe_3)CMe_2CH_2Ph$ with $ZrCl_4 \cdot 2SMe_2$ in dichloromethane followed by precipitation with dimethoxyethane (dme) gave $(C_5H_4CMe_2CH_2Ph)ZrCl_3 \cdot dme$ (**3a**) as an off-white solid. On the other hand, the reaction of $(C_5H_4SiMe_3)CMe_2Ph$ with $ZrCl_4 \cdot 2SMe_2$ was slow and did not lead to the desired product, even after prolonged reaction times.

The silylcyclopentadienyl complex $(C_5H_4SiMe_2Ph)TiCl_3$ (**4a**) was made by a different route, by treating a suspension of $Li[C_5H_4SiMe_2Ph]$ with $TiCl_4$ in light petroleum at $-78^\circ C$. The complex was obtained as long yellow needles in 49% yield.

The influence of sterically more hindered cyclopentadienyl substituents was explored by preparing the diphenylmethyl derivative $(C_5H_4CHPh_2)TiCl_3$ (**5a**) which is accessible in an analogous manner from $TiCl_4$ and $(C_5H_4CHPh_2)SiMe_3$ (Scheme 2). The complex forms orange crystals. Treatment of the trichlorides

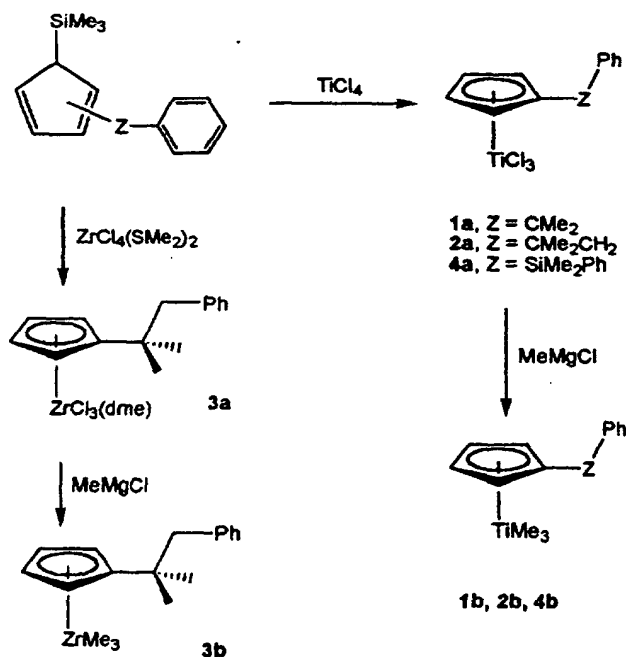


Scheme 2.

1a–4a with methylmagnesium chloride in diethyl ether at $-78^\circ C$ affords the trimethyl derivatives **1b–4b**, respectively. All four compounds form dark yellow (Ti) to red-brown (Zr) oils, which could not be induced to crystallise. All compounds were spectroscopically pure according to NMR and were unequivocally characterised, although **2b** and **4b** proved very sensitive and did not give satisfactory elemental analyses. By contrast, the reaction of **5a** with benzylmagnesium chloride gave the tribenzyl complex $(C_5H_4CHPh_2)Ti(CH_2Ph)_3$ (**5b**) as red crystals in 50% yield. The spectroscopic data of the neutral complexes are collected in Table 1.

Complexes **1a**, **4a** and **5a** gave crystals suitable for X-ray diffraction; the structures are shown in Figs. 1–3. Selected bond lengths and angles are listed in Table 2. All three chlorides are monomeric, with unexceptional geometric parameters. The complexes show the familiar piano-stool geometry. The phenyl substituents adopt a conformation roughly perpendicular to the plane of the cyclopentadienyl ring; there is no indication of either intra- or inter-molecular interaction between the aryl ring and the metal centre. The diphenylmethylcyclopentadienyl ligand in **5a** adopts a propeller arrangement; the structure resembles the recently reported rhodium complexes $LRh(PF_3)(PPr_3)$ and $LRhCl_2(PPr_3)$ [12].

The structure of the tribenzyl complex **5b** is shown in Fig. 4. The $-CHPh_2$ substituent adopts a conformation that minimises interaction with the benzyl ligands. The three benzyl ligands are η^1 -bonded, with normal $Ti-CH_2-Ph$ angles of $119.7-125.0^\circ$, unlike the related fulvalene complex $(\eta^5:\eta^5-C_{10}H_8)\{Ti(CH_2Ph)_3\}_2$ which contains differently coordinated benzyl ligands with $Ti-C-C(Ph)$ angles ranging from 90.9 to 128° , one of which is η^2 -bonded, while another shows an α -agostic interaction [13]. Although in **5b** one of the $Ti \cdots H$ distances, $Ti-H(411)$, is relatively short ($2.35(4)$ Å) and falls within the range observed for agostic interactions,



Scheme 1.

this is not borne out by the unremarkable Ti–C–C(Ph) angle of 120.0(3)°. The other Ti···H distances vary from 2.44(4) to 2.55(4) Å.

2.1. Cationic complexes

The reaction of **1b–5b** with $[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ or $\text{B}(\text{C}_6\text{F}_5)_3$ in dichloromethane was studied by NMR spectroscopy. The reaction of **1b** with a slight excess of $[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ in CD_2Cl_2 in a NMR tube at -78°C proceeded slowly but was quantitative on warming to -40°C . The spectra are recorded at this temperature. The data indicate that phenyl coordination has occurred to give the *ansa*-complex $[(\eta^5\text{-C}_5\text{H}_4\text{CMe}_2\text{-}\eta^1\text{-C}_6\text{H}_5)\text{TiMe}_2][\text{B}(\text{C}_6\text{F}_5)_4]^-$ (**6**) (Scheme 3). The signal for

the *para*-H is low-field shifted by 1.14 ppm, from δ 7.36 in the neutral precursor **1b** to δ 8.50 in **6** (Table 3). Similar trends can be observed for the *ortho* and *meta* protons of the phenyl ring. Equally indicative is the separation of the ^1H -NMR signals of the monosubstituted cyclopentadienyl rings. In the case of the *ansa*-metallocenes $\{\text{X}(\text{C}_5\text{H}_4)_2\}\text{TiCl}_2$ the separation of the two triplets increases with decreasing angle between the Cp planes, from $\text{X} = (\text{CH}_3)_3$ ($\Delta\delta = 0.04$ ppm), Me_2Ge ($\Delta\delta = 1.21$), Me_2Si ($\Delta\delta = 1.25$) to $\text{X} = \text{H}_2\text{C}$ ($\Delta\delta = 1.35$), a good indication for increasing chelate ring strain [14]. The same picture emerges in the transformation of **1b** into **6**: while the Cp protons are superimposed in the neutral complex (δ 6.39), they are separated into two sets of triplets ($\Delta\delta = 1.46$ ppm) in the cationic complex.

Table 1
NMR data of neutral titanium and zirconium half-sandwich complexes^a

Compound	Data (δ /ppm, J/Hz)
$(\text{C}_5\text{H}_4\text{CMe}_2\text{Ph})\text{TiCl}_2$ (1a)	^1H -NMR: δ 2.20 (s, 6H, Me), 7.22 (t, 2H, $J_{\text{HH}} = 2.7$, Cp), 7.39 (t, 2H, $J_{\text{HH}} = 2.7$, Cp), 7.54–7.69 (m, 5H, Ph). ^{13}C -NMR: δ 28.80 (Me), 41.00 (CMe ₂ Ph), 121.81 (Cp), 123.55 (Cp), 125.89 (<i>m</i> -C of Ph), 126.67 (<i>p</i> -C of Ph), 128.54 (<i>o</i> -C of Ph), 147.63 (<i>ipso</i> -C of Cp), 154.66 (<i>ipso</i> -C of Ph).
$(\text{C}_5\text{H}_4\text{CmePh})\text{TiMe}_3$ (1b)	^1H -NMR: δ 1.33 (s, 9H, Ti–CH ₃), 1.75 (s, 6H, CCH ₃), 6.39 (m, 4H, Cp), 7.36 (m, 1H, <i>p</i> -Ph), 7.47 (s, 2H, <i>m</i> -Ph), 7.48 (s, 2H, <i>o</i> -Ph). ^{13}C -NMR: δ 29.42 (CMe ₂), 39.74 (CMe), 62.79 (Ti–Me), 109.21 (Cp), 113.68 (Cp), 125.86 (<i>p</i> -C of Ph), 126.01 (<i>m</i> -C of Ph), 128.06 (<i>o</i> -C of Ph), 143.84 (<i>ipso</i> -C, Cp), 150.19 (<i>ipso</i> -C of Ph).
$(\text{C}_5\text{H}_4\text{CMe}_2\text{CH}_2\text{Ph})\text{TiCl}_2$ (2a)	^1H -NMR: δ 1.51 (s, 6H, Me), 2.87 (s, 2H, CH ₂), 6.81–6.85 (m, 4H, Cp), 7.20–7.30 (m, 5H, Ph). ^{13}C -NMR: δ 26.91 (Me), 38.75 (CMe ₂), 52.03 (CH ₂), 121.53 (Cp), 123.45 (Cp), 125.31 (<i>p</i> -C of Ph), 127.87 (<i>o</i> -C of Ph), 130.53 (<i>m</i> -C of Ph), 136.91 (<i>ipso</i> -C of Cp), 154.07 (<i>ipso</i> -C of Ph).
$\text{C}_5\text{H}_4\text{CMe}_2\text{CH}_2\text{Ph})\text{TiMe}_3$ (2b)	^1H -NMR: δ 1.35 (s, 9H, Ti–CH ₃), 1.36 (s, 6H, CCH ₃), 3.00 (s, 2H, CH ₂), 6.31 (t, 2H, $J_{\text{HH}} = 2.6$, Cp), 6.38 (t, 2H, $J_{\text{HH}} = 2.6$, Cp), 7.10–7.14 (m, 2H, Ph), 7.41–7.46 (m, 2H, Ph). ^{13}C -NMR: δ 27.09 (CCH ₃), 36.84 (CCH ₃), 52.44 (CH ₂), 62.86 (Ti–CH ₃), 108.94 (Cp), 113.47 (Cp), 126.03 (<i>p</i> -C, Ph), 127.45 (<i>o</i> -C, Ph), 130.68 (<i>m</i> -C, Ph), 138.26 (<i>ipso</i> -C, Cp), 143.24 (<i>ipso</i> -C, Ph).
$(\text{C}_5\text{H}_4\text{CMe}_2\text{CH}_2\text{Ph})\text{ZrCl}_2 \cdot \text{dme}$ (3a)	^1H -NMR: δ 1.51 (s, 6H, Me), 2.82 (s, 2H, CH ₂), 3.80 (s, br, 6H, OMe), 4.02 (s, br, 4H, OCH ₂), 6.43 (t, 2H, $J_{\text{HH}} = 2.5$, Cp), 6.45 (t, 2H, $J_{\text{HH}} = 2.5$, Cp), 6.78 (2H, <i>m</i> -Ph), 7.16 (m, 3H, <i>o</i> -, <i>p</i> -Ph). ^{13}C -NMR: δ 26.17 (Me), 38.56 (CMe ₂), 53.13 (CH ₂), 63.77 (OMe), 72.78 (OCH ₂), 117.78 (Cp), 117.98 (Cp), 125.99 (<i>p</i> -C of Ph), 127.40 (<i>m</i> -C of Ph), 130.71 (<i>o</i> -C of Ph), 123.11 (<i>ipso</i> -C of Cp), 146.00 (<i>ipso</i> -C of Ph).
$(\text{C}_5\text{H}_4\text{CMe}_2\text{CH}_2\text{Ph})\text{ZrMe}_3$ (3b)	^1H -NMR: δ 0.32 (s, 9H, Zr–CH ₃), 1.27 (s, 6H, CCH ₃), 2.84 (s, 2H, CH ₂), 6.18 (t, 2H, $J_{\text{HH}} = 2.6$, Cp), 6.22 (t, 2H, $J_{\text{HH}} = 2.6$, Cp), 6.93–6.98 (m, 2H, Ph), 7.22–7.27 (m, 3H, Ph). ^{13}C -NMR: δ 27.43 (Zr–CH ₃), 35.39 (CCH ₃), 45.28 (CCH ₃), 52.24 (CH ₂), 106.62 (Cp), 110.64 (Cp), 126.06 (<i>p</i> -C, Ph), 127.48 (<i>m</i> -C, Ph), 130.63 (<i>o</i> -C, Ph), 138.28 (<i>ipso</i> -C, Cp), 141.83 (<i>ipso</i> -C, Ph).
$(\text{C}_5\text{H}_4\text{SiMe}_2\text{Ph})\text{TiCl}_2$ (4a)	^1H -NMR: δ 0.68 (SiMe ₂), 7.05 (t, 2H, $J_{\text{HH}} = 2.4$, Cp), 7.25 (t, 2H, $J_{\text{HH}} = 2.4$, Cp), 7.33–7.53 (m, 5H). ^{13}C -NMR: δ –2.27 (SiMe ₂), 126.49 (Cp), 128.17 (Cp), 129.86 (<i>m</i> -C of Ph), 129.94 (<i>p</i> -C of Ph), 133.95 (<i>o</i> -C of Ph), 135.81 (<i>ipso</i> -C of Cp), 140.27 (<i>ipso</i> -C of Ph).
$(\text{C}_5\text{H}_4\text{SiMe}_2\text{Ph})\text{TiMe}_3$ (4b)	^1H -NMR: δ 0.45 (s, 6H, Si–CH ₃), 1.09 (s, 9H, Ti–CH ₃), 6.44 (m, 4H, Cp), 7.34–7.38 (m, 3H, Ph), 7.51–7.54 (m, 2H, Ph). ^{13}C -NMR: δ 1.88 (Si–CH ₃), 63.19 (Ti–CH ₃), 117.58 (Cp), 117.94 (Cp), 124.92 (<i>ipso</i> -C, Cp), 127.92 (<i>p</i> -C, Ph), 129.26 (<i>m</i> -C, Ph), 133.98 (<i>o</i> -C, Ph), 138.43 (<i>ipso</i> -C, Ph).
$(\text{C}_5\text{H}_4\text{CHPh}_2)\text{TiCl}_2$ (5a)	^1H -NMR: δ 5.82 (s, 1H, CHPh ₂), 6.74 (t, 2H, Cp), 6.96 (t, 2H, Cp), 7.17–7.36 (m, 10H, Ph). ^{13}C -NMR: δ 53.21 (CHPh ₂), 123.32, 123.70, 141.71 (Cp), 127.33, 128.84, 128.91, 147.10 (Ph).
$\text{C}_5\text{H}_4\text{CHPh}_2)\text{Ti}(\text{CH}_2\text{Ph})_2$ (5b)	^1H -NMR: δ 2.93 (s, 6H, CH ₂ Ph), 4.64 (s, 1H, CHPh ₂), 5.63 (t, 2H, Cp), 5.82 (t, 2H, Cp), 6.64 (d, 6H, <i>o</i> -benzyl), 6.88 (t, 3H, <i>p</i> -benzyl), 7.08–7.34 (m, 16H, <i>m</i> -benzyl and CHPh ₂). ^{13}C -NMR: δ 51.78 (CHPh ₂), 92.73 (CH ₂ Ph), 115.52 (Cp), 118.11 (Cp), 122.52 (<i>p</i> -C, Bz), 126.24 (<i>m</i> -C, Bz), 126.70 (<i>p</i> -C, Ph), 128.50 (<i>o</i> -C, Bz), 128.58, 128.84 (Ph), 138.52 (<i>ipso</i> -C, Cp), 143.97 (<i>ipso</i> -C, Ph), 148.05 (<i>ipso</i> -C, Bz).

^a CDCl_3 , 25°C .

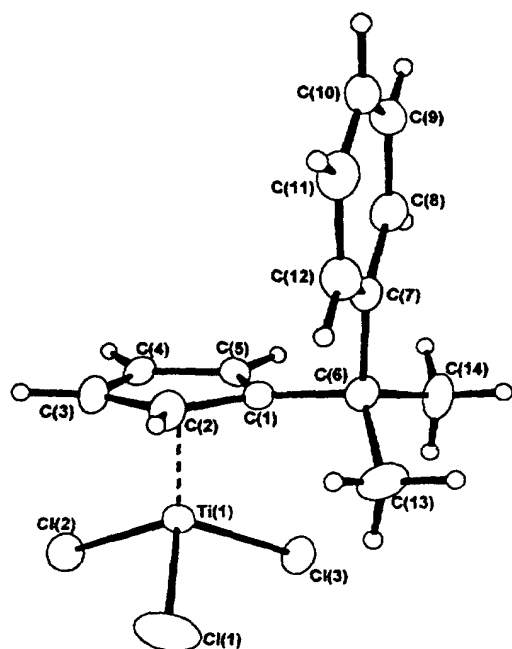


Fig. 1. Molecular structure of $(C_5H_4CMe_2Ph)TiCl_3$ (1a), showing the atomic numbering scheme. The atoms are represented by thermal ellipsoids at 40% probability level.

The reaction of **2b** with $[Ph_3C]^+[B(C_6F_5)_4]^-$ gave clean 1H - and ^{13}C -NMR spectra at $-60^\circ C$ which are consistent with the quantitative formation of $[(\eta^5-C_5H_4CMe_2CH_2-\eta^6-C_6H_5)TiMe_2]^+[B(C_6F_5)_4]^-$ (**7a**). This complex appears more stable than **6**. The resonances for the *para* and *meta* protons of the phenyl ring are clearly resolved at δ 8.73 (*p*-H) and δ 8.43 (*m*-H).

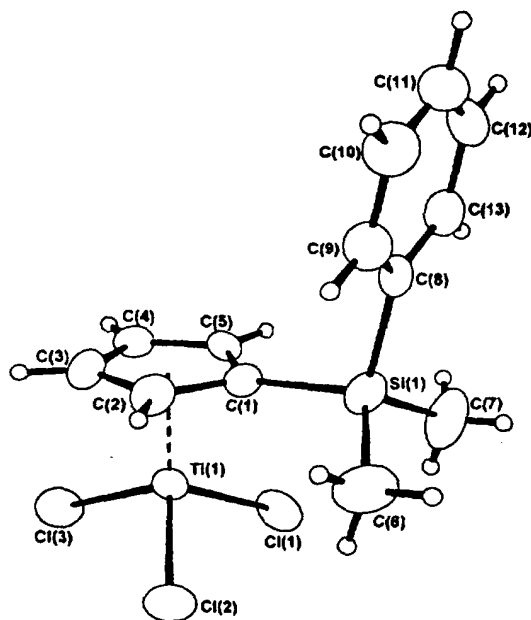


Fig. 2. Molecular structure of $(C_5H_4SiMe_2Ph)TiCl_3$ (4a).

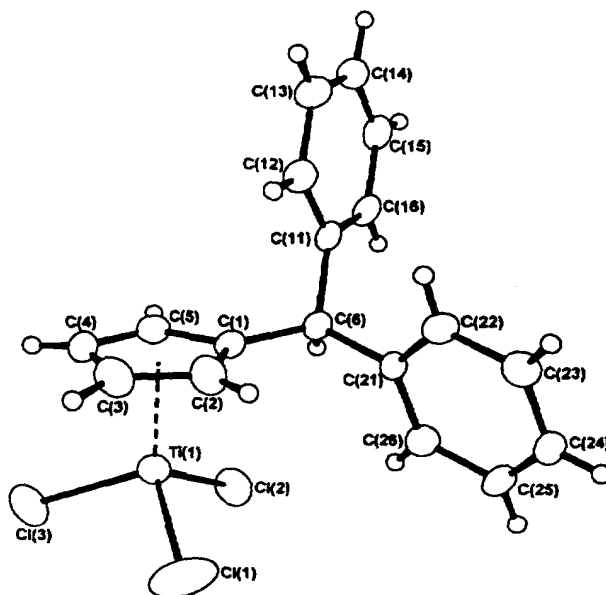


Fig. 3. Molecular structure of $(C_5H_4CHPh_2)TiCl_3$ (5a).

The chemical shift difference for the Cp protons is less pronounced, indicating the reduced strain of the $-CMe_2CH_2-$ bridge.

The reaction of **2b** with $B(C_6F_5)_3$ cleanly gives $[(\eta^5-C_5H_4CMe_2CH_2-\eta^6-C_6H_5)TiMe_2]^+[MeB(C_6F_5)_3]^-$ (**7b**). The structure of the cation is identical to **7a**, with a non-coordinated counteranion. In an analogous manner, the zirconium complex **3b** affords $[(\eta^5-C_5H_4CMe_2CH_2-\eta^6-C_6H_5)ZrMe_2]^+[B(C_6F_5)_4]^-$ (**8a**), while the reaction with $B(C_6F_5)_3$ gives the corresponding $[MeB(C_6F_5)_3]^-$ compound **8b**, although in this case unidentified side-products were also in evidence.

Table 2
Selected bond lengths (Å) and angles ($^\circ$) of titanium trichloride complexes

Compound	1a	4a	5a
<i>Bond lengths</i>			
Ti–Cl(1)	2.2151(16)	2.227(2)	2.227(2)
Ti–Cl(2)	2.2317(15)	2.213(2)	2.221(2)
Ti–Cl(3)	2.2368(14)	2.210(2)	2.2367(13)
Ti–C(1)	2.398(3)	2.343(5)	2.391(3)
Ti–C(2)	2.3342(4)	2.327(6)	2.344(4)
Ti–C(3)	2.308(4)	2.340(6)	2.308(4)
Ti–C(4)	2.322(3)	2.334(6)	2.314(4)
Ti–C(5)	2.358(3)	2.344(5)	2.340(4)
C(1)–C(6)	1.532(5)		1.512(5)
C(1)–Si(1)		1.892(6)	
<i>Bond angles</i>			
Cl(1)–Ti–Cl(2)	102.43(5)	101.99(9)	104.99(6)
Cl(1)–Ti–Cl(3)	103.93(5)	102.08(9)	101.92(6)
Cl(2)–Ti–Cl(3)	102.38(4)	103.39(9)	101.90(5)
C(1)–C(6)–C(7)	103.5(3)		
C(1)–Si–C(8)		105.1(3)	

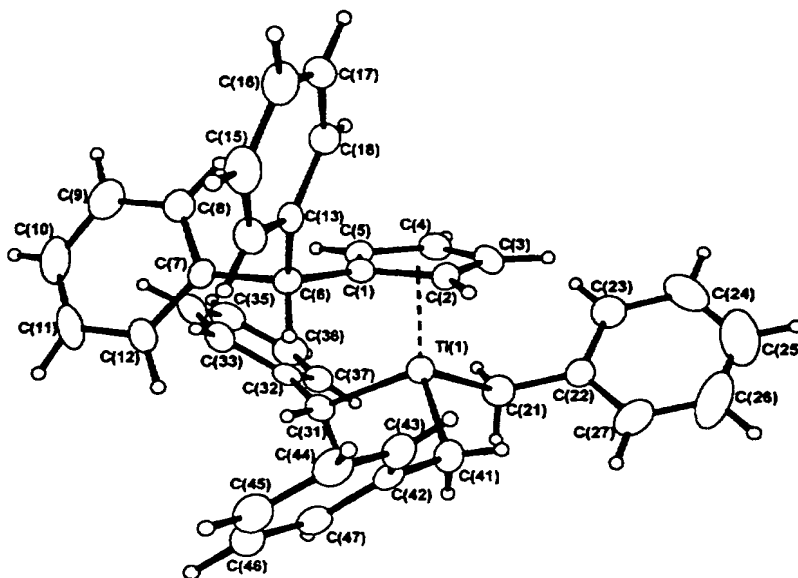


Fig. 4. Molecular structure of $(C_5H_4CHPh_2)Ti(CH_2Ph)_2$ (**5b**). Selected bond lengths (Å) and angles (°): Ti–C(21) 2.129(6), Ti–C(31) 2.111(5), Ti–C(41) 2.122(5), Ti–H(411) 2.35(4), Ti–H(412) 2.55(4), Ti–C(21)–C(22) 119.7(4), Ti–C(31)–C(32) 125.0(3), Ti–C(41)–C(42) 120.0(3).

In contrast to the reactions with carbon-bridged compounds, no product could be identified in the reaction of $(C_5H_4SiMe_2Ph)TiMe_3$ (**4a**) with $[Ph_3C]^+[B(C_6F_5)_4]^-$. The spectra indicated extensive decomposition, even at $-60^\circ C$. The same result was obtained when **4a** was treated with $B(C_6F_5)_3$; again complex spectra were recorded which could not be assigned.

As is well known, cationic Group 4 benzyl complexes can be stabilised in several different ways not open to methyl compounds [15]. For example, one or both of the benzyl ligands in a cation $[Cp^R M(CH_2Ph)_2]^+$ may be η^2 -bonded. In $[Cp^*Zr(CH_2Ph)_2]^+$ both η^3 - and η^2 -coordination has been observed [16], while for $[(C_5H_3Bu_2)Zr(CH_2Ph)_2]^+$ η^1 - and η^2 -bonding has been suggested [17]. If the cation was generated by benzyl abstraction with $B(C_6F_5)_3$, π -coordination of the $[PhCH_2B(C_6F_5)_3]^-$ anion is prevalent [6,7]. On the other hand, coordination of a neutral arene to a cationic benzyl complex has to our knowledge not been observed.

Treatment of a solution of the benzyl complex **5b** in CD_2Cl_2 at $-60^\circ C$ with $[Ph_3C^-][B(C_6F_5)_4]^-$ gives the ionic product $[\eta^5-C_5H_4CHPh_2]Ti(CH_2Ph)_2[B(C_6F_5)_4]$ (**9**). The phenyl region of the 1H -NMR spectrum is difficult to assign because of the superimposition of the signals for the $CHPh_2$ substituent, the benzyl ligands, and the Ph_3CCH_2Ph by-product. Indicative for the structure of the product are, however, the changes in the cyclopentadienyl resonances. In **5b** these are observed at δ 5.63 and 5.82 ($\Delta\delta = 0.19$ ppm), whereas in **9** they are found at δ 4.92 and δ 6.88 ($\Delta\delta = 1.96$ ppm), a clear indication of the formation of a comparatively

strained chelate ring by π -coordination of one of the phenyl rings.

The compound exhibits fluxionality. First, the two $CHPh_2$ phenyl rings can interchange. A second process that can be envisaged involves a change in the coordination mode of the benzyl ligands which can displace the $CHPh_2$ substituent and become η^2 -bonded. If that happens, one should expect to see the appearance of diastereotopic benzyl methylene groups. This is indeed observed. On lowering the temperature to $-90^\circ C$ a second isomer of **9** is observed: the broad peak for the benzylic CH_2 groups at δ 3.05 splits into two sets of broadened doublets at δ 3.46 and δ 2.40, with a geminal coupling constant of 9 Hz. The difference in Cp resonances is much smaller than in the major isomer, $\Delta\delta = 0.86$ ppm, in agreement with a less strained structure. The data are consistent with an equilibrium between an *ansa*-complex with η^1 -benzyl ligands and an η^2 -benzyl isomer where the π -phenyl coordination is weakened or lost (Scheme 4).

Several attempts were made to isolate ionic *ansa*-aryl complexes from any of these reactions at a preparative scale. However, they met with little success, even in the case of the $-CMe_2CH_2-$ compounds which are comparatively stable in solution. Orange to brown powders were obtained which could not be induced to crystallise and which gave variable elemental analyses.

2.2. Propene polymerisation

One of the incentives for this work was to study the influence of reversible phenyl coordination on the activity of polymerisation catalysts and on polymer molecu-

lar weights. As noted earlier, the system $\text{Cp}^*\text{TiMe}_3/\text{B}(\text{C}_6\text{F}_5)_3$, without a pendant ligand, gives high molecular weight elastomeric polypropene in either toluene or light petroleum [10,11]. On the other hand, methylaluminoxane activated $(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{Ph})\text{TiCl}_3$ shows comparatively modest activity for ethene polymerisation, whereas pendant amino groups $-\text{CH}_2\text{CH}_2\text{NR}_2$ have an enhancing effect [18].

The effect of a comparatively weakly coordinated pendant ligand such as phenyl on the behaviour of a polymerisation catalyst is difficult to predict. A reversibly coordinated phenyl ligand might either act to protect the growing polymer chain from $\beta\text{-H}$ elimination by stabilising a 16-electron resting state, thus giving longer polymer chains and narrower molecular weight distributions, or it might compete with monomer take-up to such an extent that the rate of chain termination becomes competitive, possibly resulting in oligomers rather than polymers.

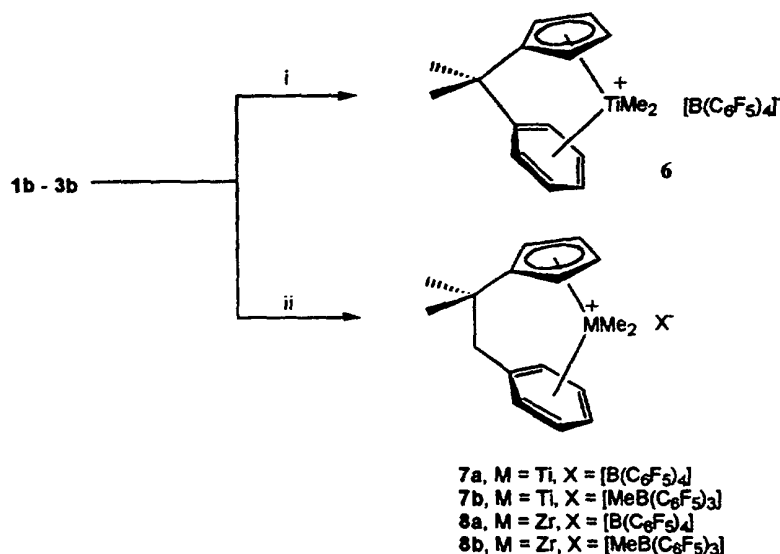
Activation of a propene-saturated toluene solution of **2b** with an equimolar amount of $\text{B}(\text{C}_6\text{F}_5)_3$ leads to the formation of atactic polypropene (Table 4). Except for the polymerisation carried out at 0°C , the polymer did not precipitate upon methanol addition. In sharp contrast to the system $\text{Cp}^*\text{TiMe}_3/\text{B}(\text{C}_6\text{F}_5)_3$ which gives molecular weights of the order of $0.5\text{--}2 \times 10^6$ at high productivities (Table 4, entries 9 and 10), the polymer formed with **2b**/ $\text{B}(\text{C}_6\text{F}_5)_3$ is of low molecular weight, and the polydispersities are comparatively broad. Broad polydispersities might arise either from partial decomposition of the catalyst, or be the result of a comparatively slow equilibrium between dormant (precursor) and active states.

Although in NMR reactions attempts to generate

characterisable cations from **4b** were not successful, mixtures of **4b** and showed higher catalytic activity than **2b**. On the other hand, polymer molecular weights were even lower, even at -20°C , while the molecular weight distributions were narrower. The lowest activity was observed for the benzyl complex **5b**. It appears to be thermally unstable under catalytic conditions; activity decreased from -20°C to 0°C , while only trace amounts of polymer were obtained at 20°C .

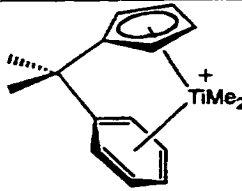
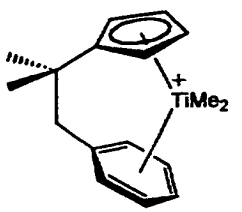
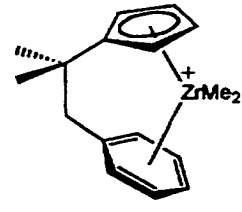
2.3. Conclusions

Pendant phenyl moieties coordinate to cationic Group 4 metal centres to give comparatively stable *ansa*-arene complexes of the type $[(\text{Cp}-\text{X}-\text{Ph})\text{MR}_2]^+$. This type of arene coordination is preferred over coordination to anions such as $[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$, even in the case of titanium where the formation of $\text{Ti}-\mu\text{-MeB}(\text{C}_6\text{F}_5)_3$ zwitterions is well documented [8,11,19]. Low-temperature NMR studies suggest that in the case of the benzyl complexes at low temperature there is competition between the *ansa* structure and η^2 -coordination of benzyl ligands. Assuming η^6 -arene coordination, the $[(\text{Cp}-\text{X}-\text{Ph})\text{MR}_2]^+$ cations represent 16-electron resting states of active polymerisation catalysts. Presumably as the result of preferential arene coordination, mixtures of $(\text{Cp}-\text{X}-\text{Ph})\text{MR}_2$ and $\text{B}(\text{C}_6\text{F}_5)_3$ are less active in propene polymerisations than systems with non-chelating ligands, and chain termination is enhanced. On the other hand, chain termination is not as frequent as with Cp_2ZrCl_2 /methylaluminoxane catalysts which give low-molecular-weight propene oligomers [20].



Scheme 3. Reagents and conditions: (i) $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$; (ii) **a** = $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$, **b** = $\text{B}(\text{C}_6\text{F}_5)_3$.

Table 3
NMR data of cationic titanium and zirconium complexes^a

Compound	Data (δ ppm, J Hz)
$[(C_5H_4CMe_2Ph)TiMe_2][B(C_6F_5)_4]$ (6) 	¹ H-NMR: δ 0.97 (s, 6H, Ti-Me), 1.65 (s, 6H, CMe), 5.91 (t, 2H, Cp), 7.04 (d, 2H, <i>o</i> -Ph), 7.37 (t, 2H, Cp), 8.50 (m, 3H, Ph). ¹³ C-NMR: δ 30.04 (CMe), 41.15 (CMe), 68.14 (Ti-Me), 113.11 (Cp), 124.92 (Cp), 126.12 (<i>o</i> -C of Ph), 128.45 (<i>p</i> -C of Ph), 140.12 (<i>m</i> -C of Ph).
$[(C_5H_4CMe_2CH_2Ph)TiMe_2][MeB(C_6F_5)_3]$ (7b) 	¹ H-NMR: δ 0.42 (br, 3H, B-Me), 0.64 (s, 6H, Ti-Me), 1.30 (s, 6H, CMe ₂), 2.80 (s, 2H, CH ₂), 6.18 (s, 2H, Cp), 7.15 (s, 2H, Cp), 7.21 (d, 2H, <i>o</i> -Ph), 8.41 (t, 2H, <i>m</i> -Ph), 8.71 (t, 1H, <i>p</i> -Ph). ¹³ C-NMR: δ 9.47 (B-Me), 30.30 (CMe), 41.04 (CMe), 47.80 (CH ₂), 64.62 (Ti-Me), 114.00 (Cp), 123.47 (Cp), 129.00 (<i>o</i> -C of Ph), 131.45 (<i>p</i> -C of Ph), 137.75 (<i>m</i> -C of Ph), 141.24 (<i>ipso</i> -C of Cp), 142.68 (<i>ipso</i> -C of Ph).
$[(C_5H_4CMe_2CH_2Ph)ZrMe_2][MeB(C_6F_5)_3]$ (8b) 	¹ H-NMR: δ 0.18 (s, 6H, Zr-CH ₃), 0.46 (br, 3H, B-CH ₃), 1.40 (s, 6H, CCH ₃), 3.21 (s, 2H, CH ₂), 6.27 (t, 2H, Cp), 6.65 (t, 2H, Cp), 7.60 (d, 2H, <i>o</i> -Ph), 8.19 (t, 1H, <i>p</i> -Ph), 8.33 (t, 2H, <i>m</i> -Ph). ¹³ C-NMR: δ 9.55 (B-CH ₃), 31.63 (CCH ₃), 40.89 (CCH ₃), 42.96 (Zr-CH ₃), 48.70 (CH ₂), 109.94 (Cp), 117.64 (Cp), 129.13 (<i>p</i> -C of Ph), 130.15 (<i>o</i> -C of Ph), 135.82 (<i>m</i> -C of Ph), 137.76 (<i>ipso</i> -C of Cp), 144.17 (<i>ipso</i> -C of Ph).

^a CD₂Cl₂, -60°C, 300 MHz. The data for 7a and 8a are omitted since they are essentially identical to those given for 7b and 8b.

3. Experimental

3.1. General procedures

All experiments were carried out under nitrogen atmosphere by using standard Schlenk techniques. Solvents were dried over sodium (toluene, low in sulphur), sodium-potassium alloy (diethyl ether, light petroleum, b.p. 40–60°C) sodium-benzophenone (THF) and calcium hydride (dichloromethane). NMR solvents were dried over activated 4 Å molecular sieves and degassed by several freeze-thaw cycles. NMR spectra were recorded using Bruker ARX250, DPX300 or Jeol EX270 spectrometers and referenced to residual solvent peaks. Chemical shifts are quoted in ppm relative to TMS. Propene (BOC) was passed through P₂O₅ and activated molecular sieves and condensed onto Et₂AlOHex prior to use.

3.2. Preparation of C₅H₄(SiMe₃)CMe₂Ph

To a solution of phenyllithium (214 mmol) in 200 cm³ diethyl ether at -78°C was added dropwise 22.7 g (214 mmol) of dimethylfulvene. The mixture was al-

lowed to warm to r.t. and stirred for 20 min. The resulting white suspension was slowly added to a mixture of 23.2 g (214 mmol) of trimethylchlorosilane in 120 cm³ THF. The reaction mixture was stirred overnight, poured onto ice water and extracted with light petroleum. The organic phase was dried over magnesium sulphate, the volatiles were removed under vacuum to yield a yellow oil which was distilled at reduced pressure. Yield: 32.6 g (124.8 mmol, 58.3%), b.p. 82–100°C/0.1 torr. ¹H-NMR (300 MHz, 22°C, CDCl₃): δ 0.29 (s, 9 H, SiMe₃), 1.87 (s, 6 H, CMe₂), 6.70–6.47 (m, 4 H, C₅H₄), 7.64–7.43 (m, 5 H, Ph).

3.3. Preparation of C₅H₄(SiMe₃)CMe₂CH₂Ph

To a solution of benzylmagnesium chloride (220 mmol) in 350 cm³ THF was added 22.7 g (214 mmol) of dimethylfulvene over a period of 1 h at r.t. The reaction mixture was stirred overnight and added to a solution of 23.2 g (214 mmol) of trimethylchlorosilane in 100 cm³ THF at r.t. The colour changed to orange and a precipitation formed. After stirring for 1 h the mixture was poured onto ice water and extracted with light petroleum. The organic phases was dried over magne-

sium sulphate and the volatiles were removed in vacuo to yield a yellow oil which was distilled under reduced pressure, b.p. 92–93°C/0.01 torr. $^1\text{H-NMR}$ (250 MHz, CDCl_3): δ 0.05 (s, 9 H, SiMe_3), 1.24 (s, 6 H, CMe_2), 2.84 (s, 2 H, CH_2), 6.77–6.08 (m, 4 H, C_5H_4), 7.27–7.11 (m, 5 H, Ph).

3.4. Preparation of $\text{C}_5\text{H}_5\text{SiMe}_2\text{Ph}$

The compound was made by a modification of a literature procedure [21]. A solution of sodium cyclopentadienide (146 mmol) in 200 cm^3 THF was added to a solution of 25 g (146 mmol) of chlorodimethylphenylsilane in 180 cm^3 THF at 0°C. The reaction mixture was stirred for 20 min at r.t., poured onto ice water and extracted with petroleum. Colourless oil, yield: 24.2 g (120.8 mmol, 82.7%), b.p. 60–80°C/0.1 torr.

3.5. Preparation of diphenylmethylcyclopentadiene

To a solution of 100 g (0.5 mol) of chlorodiphenylmethane in 200 cm^3 THF at -78°C was added NaCp (0.5 mol) in 200 cm^3 THF. The reaction mixture was warmed to r.t., stirred for 30 min, poured onto ice water– NH_4Cl and worked up as described above. Orange oil, yield: 30 g (129 mmol, 25.8%), b.p. 125–145°C/0.01 torr. $^1\text{H-NMR}$ (89 MHz, 28.8°C , CDCl_3): δ 1.29 (s, 1 H, CHPh_2), 5.17 (m, 1 H, Cp–H), 6.4–5.79 (m, 4 H, C_5H_4), 7.49–6.90 (m, 10 H, Ph).

3.6. Preparation of $\text{C}_5\text{H}_4(\text{SiMe}_3)\text{CHPh}_2$

To 10.95 g (47.2 mmol) $\text{C}_5\text{H}_4\text{CHPh}_2$ in 200 cm^3 THF was added at -78°C 18.9 cm^3 (47.2 mmol) of 2.5 M butyllithium. The colour changed to red. The reaction mixture was warmed to r.t., stirred for 1 h and added slowly to a mixture of 5.13 g (47.2 mmol) of chlorotrimethylsilane in 100 cm^3 THF at -78°C . The blue mixture turned yellow on warming to r.t. and was worked up as above. Removal of the solvent in vacuo yielded a waxy solid, yield: 11.0 g (36.1 mmol, 76%).

$^1\text{H-NMR}$ (250 MHz, CDCl_3 , 20°C): δ 0.02 (s, 9H, SiMe_3); 5.29 (s, 1H, CHPh_2); 5.8 (m, 2H, Cp); 6.5 (m, 2H, Cp); 7.21–7.38 (m, 10H, Ph).

3.7. Preparation of $(\text{C}_5\text{H}_4\text{CMe}_2\text{Ph})\text{TiCl}_3$ (1a)

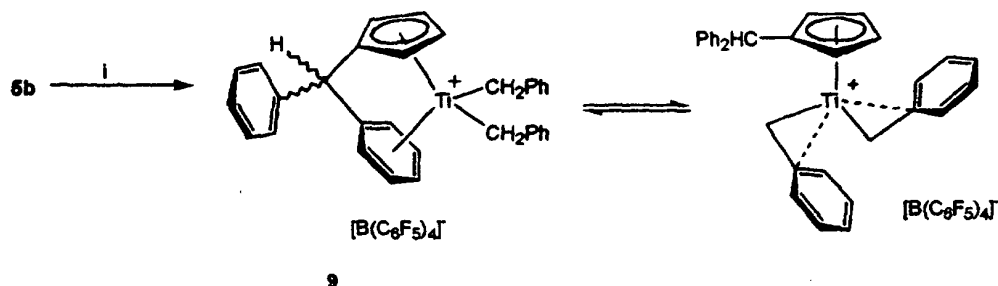
A solution of 7.69 g (30 mmol) of $\text{C}_5\text{H}_4(\text{SiMe}_3)\text{CMe}_2\text{Ph}$ in 10 cm^3 CH_2Cl_2 was added to a solution of 5.69 g (30 mmol) of TiCl_4 . The colour changed to dark red. The mixture was stirred overnight and the solvent removed to yield a dark-red oil which solidified after 1 day. The product was recrystallised from 10 cm^3 CH_2Cl_2 at -16°C to give orange crystals suitable for X-ray diffraction. A second batch of crystals was obtained from the mother liquor. Combined yield: 5.63 g (17.4 mmol, 57.8%). Anal.: $\text{C}_{14}\text{H}_{15}\text{Cl}_3\text{Ti}$ found (calc.): C, 50.0 (49.8); H, 4.5 (4.5); Cl, 31.3 (31.5)%.

3.8. Preparation of $(\text{C}_5\text{H}_4\text{CMe}_2\text{Ph})\text{TiMe}_3$ (1b)

To a solution of 12.9 g (38.1 mmol) of $(\text{C}_5\text{H}_4\text{CMe}_2\text{Ph})\text{TiCl}_3$ in 250 cm^3 diethyl ether at -78°C was added dropwise 38.1 cm^3 (114.3 mmol) of 3 M MeMgCl in Et_2O . The colour changed from red to yellow. The reaction mixture was warmed to 0°C and the solvent removed in vacuo. The residue was extracted with light petroleum and centrifuged. Evaporation of the solvent yielded a dark-yellow oil which could not be crystallised, yield: 3.22 g (11.7 mmol, 39%). For subsequent reactions a 1.17 M stock solution of 1b in light petroleum was used. Anal.: $\text{C}_{17}\text{H}_{24}\text{Ti}$ found (calc.): C, 73.2 (73.9); H, 8.9 (8.8)%.

3.9. Preparation of $(\text{C}_5\text{H}_4\text{CMe}_2\text{CH}_2\text{Ph})\text{TiCl}_3$ (2a)

To 3.3 cm^3 (30 mmol) TiCl_4 in 130 cm^3 dichloromethane was slowly added at r.t. a solution of 8.11 g (30 mmol) of $\text{C}_5\text{H}_4(\text{SiMe}_3)\text{CMe}_2\text{CH}_2\text{Ph}$ in 20 cm^3 dichloromethane. The red mixture was stirred for 2 h. The volatiles were removed in vacuo to yield a dark red oil which could not be crystallised. Yield: 9.3 g (26.5 mmol, 88%).



Scheme 4. Reagents and conditions: (i) $[\text{C}_6\text{H}_5]_3[\text{B}(\text{C}_6\text{F}_5)_4]$.

Table 4

Propene polymerisation with titanium half-sandwich complexes and $B(C_6F_5)_3$ in toluene

Entry	Precursor complex	Ti (μmol)	B (μmol)	Temp. ($^{\circ}\text{C}$)	Time (min)	Mass (mg) ^a	Productivity ^a	$M_n \times 10^{-3}$	M_w/M_n
1	2b	40	40	0	3	164.3	6.4	406	14.8
2	2b	40	40	20	3	230.3 ^b	16.2	124.5	5.8
3	2b	40	40	40	3	161.8 ^b	18.8	54.8	3.5
4	2b	40	40	60	3	82.5 ^b	16.0	23	3.7
5	4b	20	20	0	1	324	76	28.2	2.8
6	4b	20	20	–20	1	295	33	36.6	2.7
7	5b	20	20	0	10	150	3.5	36.6	3.5
8	5b	20	20	–20	1	422	47.6	129	3.3
9	Cp^*TiMe_3	20	20	0	1	1366	276	518	2.9
10	Cp^*TiMe_3	20	20	–45	2	3470	520	2275	2.0

^a In 10^4 g PP (mol Ti)^{–1} [C_3H_6]^{–1} h^{–1} bar^{–1}.^b Polymer isolated by solvent evaporation overnight.

3.10. Preparation of $(C_5H_4CMe_2CH_2Ph)TiMe_3$ (2b)

Following the procedure for 1b, methylation of 9.3 g (26.5 mmol) of 2a with 26.5 cm³ (79.4 mmol) 3 M MeMgCl afforded as a dark yellow oil. Yield: 4.4 g (15.3 mmol, 58%). The compound was pure by NMR but did not give consistent elemental analyses.

3.11. Preparation of $(C_5H_4CMe_2CH_2Ph)ZrCl_3 \cdot dme$ (3a)

A solution of 10.72 g (30 mmol) of $ZrCl_4 \cdot 2SMe_2$ in 120 cm³ dichloromethane was treated with 8.11 g (30 mmol) $C_5H_4(SiMe_3)CMe_2CH_2Ph$ in 20 cm³ dichloromethane at 0 $^{\circ}\text{C}$. The mixture was stirred overnight, 20 cm³ dme were added, the solution was concentrated and cooled to –30 $^{\circ}\text{C}$. A solid formed which was filtered off, washed with 4 \times 5 cm³ dme at –30 $^{\circ}\text{C}$ and dried under vacuum. An off-white solid was obtained, yield: 6.41 g (13 mmol, 43%). Anal.: $C_{19}H_{27}Cl_3O_2Zr$ found (calc.): C, 46.1 (47.1); H, 5.8 (5.6); Cl, 22.8 (21.9)%.

3.12. Preparation of $(C_5H_4CMe_2CH_2Ph)ZrMe_3$ (3b)

Following the procedure for 1b, compound 3b was obtained from 6.41 g (13 mmol) of 3a and 13 cm³ (39.7 mmol) of MeMgCl as a dark red–brown oil, yield: 3.6 g (10.7 mmol, 83%). Anal.: $C_{18}H_{26}Zr$ found (calc.): C, 63.9 (64.8); H, 6.9 (7.8)%.

3.13. Preparation of $(C_5H_4SiMe_2Ph)TiCl_3$ (4a)

To 6.01 g (30 mmol) of $C_5H_4SiMe_2Ph$ in 120 cm³ light petroleum was added 18.75 cm³ (30 mmol) butyllithium. A white precipitate formed. The reaction mixture was stirred 90 min at r.t., filtered and washed with light petroleum. The product was suspended in

120 cm³ petroleum and cooled to –78 $^{\circ}\text{C}$. A solution of 3.3 cm³ (30 mmol) $TiCl_4$ in 5 cm³ light petroleum was added slowly, the mixture was stirred for 3 h, warmed to –60 $^{\circ}\text{C}$ and filtered. Another aliquot of petroleum was added and the suspension warmed to 40 $^{\circ}\text{C}$ and filtered. The filtrate was stored at –16 $^{\circ}\text{C}$ to yield long, yellow needles which were suitable for X-ray diffraction. Yield: 5.21 g (14.6 mmol, 49%). Anal.: $C_{13}H_{15}Cl_3SiTi$ found (calc.): C, 44.3 (44.2); H, 4.0 (4.3); Cl, 30.2 (30.1)%.

3.14. Preparation of $(C_5H_4SiMe_2Ph)TiMe_3$ (4b)

Treatment of 4.26 g (12 mmol) of 4a in 180 cm³ diethyl ether at –78 $^{\circ}\text{C}$ with 12.0 cm³ (36 mmol) methylmagnesium chloride in THF led to a colour change to bright yellow. The reaction mixture was stirred for 1 h at –78 $^{\circ}\text{C}$ and slowly warmed to 0 $^{\circ}\text{C}$. The volatiles were removed at this temperature, the residue was extracted with 120 cm³ light petroleum and centrifuged. Removal of the solvent gave a dark yellow oil, yield: 2.3 g (7.9 mmol, 65.5%). The compound was spectroscopically pure, though the analyses were affected by its sensitivity to hydrolysis. Anal.: $C_{16}H_{24}SiTi$ found (calc.): C, 62.1 (65.7); H, 8.1 (8.3)%.

3.15. Preparation of $(C_5H_4CHPh_2)TiCl_3$ (5a)

To 7.0 g (23 mmol) $C_5H_4(SiMe_3)CHPh_2$ in 20 cm³ toluene was added 4.4 g (23 mmol) $TiCl_4$ in 80 cm³ toluene. The colour changed to dark red and the reaction was stirred for 2 h. Removal of the solvent yielded a green solid, which was washed with 2 \times 100 cm³ light petroleum and extracted with 30 cm³ CH_2Cl_2 . Concentration of the filtrate orange crystals suitable for X-ray crystallography. Yield: 2.35 g (6.1 mmol, 27%). Anal.: $C_{18}H_{15}Cl_3Ti$ found (calc.): C, 57.4 (56.1); H, 4.1 (3.9); Cl, 26.3 (27.6)%.

Table 5
Crystal data for compounds 1a, 4a, 5a and 5b

	1a	4b	5a	5b
Formula	C ₁₄ H ₁₅ Cl ₃ Ti	C ₁₃ H ₁₅ Cl ₃ SiTi	C ₁₈ H ₁₅ Cl ₃ Ti	C ₃₉ H ₁₆ Ti
<i>M</i>	337.51	353.59	385.55	552.58
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1
<i>a</i> (Å)	12.375(5)	7.972(4)	8.979(3)	11.228(3)
<i>b</i> (Å)	11.632(5)	10.594(3)	19.565(5)	11.299(4)
<i>c</i> (Å)	21.205(5)	19.296(3)	10.511(4)	13.497(4)
α (°)	90	90	90	75.24(3)
β (°)	91.633(5)	97.39(2)	110.75(3)	85.54(3)
γ (°)	90	90	90	66.73(2)
<i>U</i> (Å ³)	3051(2)	1616.1(10)	1726.7(10)	1520.6(8)
<i>T</i> (K)	298(2)	298(2)	298(2)	233(2)
<i>Z</i>	8	4	4	2
<i>D</i> _{calc} (g cm ^{−3})	1.469	1.453	1.483	1.207
μ (Mo–K α) (mm ^{−1})	1.066	1.080	0.952	0.307
Reflections collected/unique	5631/5365	2727/2525	3044/3044	5264/4226
<i>R</i> _{int} ^a	0.0256	0.0528	–	0.0445
<i>wR</i> ₂ ^b	0.1047	0.1141	0.1194	0.1184
<i>R</i> ₁ (<i>I</i> > 2 σ (<i>I</i>)) ^c	0.0359	0.0423	0.0407	0.0490

^a $R_{\text{int}} = \Sigma |F_o^2 - F_o^2(\text{mean})| / \Sigma |F_o^2|$ for those reflections measured more than once.

^b $wR_2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{0.5}$.

^c $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. Note: structures refined against F^2 using all data; *R*₁ for 'observed' data is calculated only for comparison with other structures refined against *F*.

3.16. Preparation of (C₅H₄CHPh₂)Ti(CH₂Ph)₃ (5b)

The compound was prepared from 2.35 g (6.1 mmol) (C₅H₄CHPh₂)TiCl₃ and 20 mmol benzylmagnesium chloride. The colour changed to orange. The reaction mixture was stirred overnight. Removal of volatiles gave a dark-red solid which was extracted with 230 cm³ hot petroleum. Cooling the filtrate slowly to −30°C yielded red crystals. A second crop was obtained from the mother liquor. Yield: 1.68 g (3 mmol, 50%). Anal.: C₃₉H₃₆Ti found (calc.): C, 84.6 (84.8); H, 6.9 (6.6)%.

3.17. Generation of cationic complexes

About 0.1 mmol of the titanium or zirconium trialkyl complex was dissolved in 0.25 cm³ CD₂Cl₂, transferred to a NMR tube and cooled to −78°C. 0.11 mmol of either B(C₆F₅)₃ or [CPh₃][B(C₆F₅)₄] was dissolved in 0.3 cm³ CD₂Cl₂ and mixed with the metal alkyl solution. The colour darkened to orange. The sample was immediately inserted into the pre-cooled (−60°C) spectrometer probe.

Attempts to isolate the ionic products from analogous reactions at a preparative scale gave orange to brown solids, which could not be crystallised.

3.18. Propene polymerisations

Polymerisations were conducted in a flame-dried all-glass reactor. Stock solutions (ca. 10^{−5} M) of metal alkyls were freshly prepared in toluene. Polymerisations were

carried out by equilibrating a given amount of purified and degassed solvent at the stated temperature with the monomer at 1 bar. Polymerisation was initiated by injecting an aliquot of the metal alkyl stock solution followed by the injection of an equimolar amount of either B(C₆F₅)₃ or [CPh₃][B(C₆F₅)₄] and terminated by injecting 2 cm³ of methanol. The polymer was precipitated with large amounts of methanol and dried at 60°C for 12 h. In the case of low-molecular-weight polymers the toluene–methanol mixture was allowed to evaporate and the residue recovered for analysis.

3.19. X-ray crystallography

Data were collected on a Rigaku AFC7R diffractometer using graphite-monochromated Mo–K α radiation ($\lambda = 0.71073$ Å). Structures were solved by direct methods, and refined against all data by full-matrix least-squares on F^2 , with anisotropic displacement parameters assigned to all non-hydrogen atoms. The SHELXTL suite of programs [22] was used for all calculations. Crystal data, and further details of data collection and refinement, are summarised in Table 5.

4. Supplementary material

The Cambridge Crystallographic Data Centre deposition numbers for complexes 1a, 4a, 5a and 5b are CCDC-132427, -132428, -132429 and -133204. Copies of

this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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